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A NEW METHOD FOR THE ANALYSIS OF COMMERCIAL PHENOLS.

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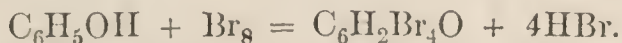
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THE methods hitherto adopted for the estimation of phenols may be divided into three classes, depending on—

- I. The precipitation of bromine derivatives.
- II. The precipitation of iodine derivatives.
- III. Direct titration with alkalis.

I. The earliest method under the first heading is that suggested by Landolt (*Berichte*, IV., 770), and consisted simply in the precipitation of the phenol by bromine. In the case of ordinary phenol, the compound precipitated has a composition corresponding with the formula $C_6H_2Br_4O$. This older method has since undergone various modifications, suggested by Koppeschaar (*Zeits. f. analyt. Chem.* **25**, 162), Weinreb and Bondi (*Wiener Monatsheft f. Chem.* **6**, 506), Kossler and Penny (*Hoppe Seyler's Zeit. f. physiol. Chem.* **17**, 133), Toth (*Zeit. f. analyt. Chem.* **25**, 162). The method adopted by Koppeschaar has become standard, and originally consisted in adding to an aqueous solution of the phenol, a solution of bromine in caustic soda in the presence of hydrochloric acid. After standing for some time, the excess of bromine is estimated by the addition of potassium iodide, and the titration of the iodine thus set free by standard thiosulphate solution. The reactions taking place may be represented by the equations:—



It will be seen, therefore, that each molecule of phenol will correspond to six, and not eight atoms of bromine, the tetrabromophenol originally precipitated being partially decomposed by the potassium iodide.

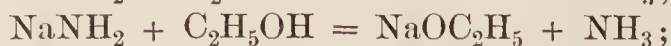
The method of Koppeschaar has since been modified in various smaller details. Giacosa (*Zeits. f. physiol. Chem.* **6**, 45) adds bromine water to an aqueous solution of the phenol, until the supernatant liquid commences to turn starch-potassium iodide paper blue. Chandelon (*Bull. Soc. Chim.* **38**, 75) adds a dilute phenol solution to potassium hypobromite solution until the liquid no longer acts on starch potassium iodide paper. (Compare also Seubert, *Jahresbericht der Chem.* 1881, 1204.)

II. Messinger and Vortmann (Ber. XXII., 2313) have shown that when iodine dissolved in potassium iodide is added to a strongly alkaline solution of a phenol warmed to 50°—60° C., coloured iodine compounds of a characteristic nature are formed. Ordinary phenol gives a product the composition of which corresponds to the formula $C_6H_3I_3O$. Thymol and other phenols give analogous compounds. By estimating the amount of iodine absorbed by various phenols, Messinger and Vortmann have devised a quantitative method for their estimation, which seems to have a fairly general application (Ber. XXIII., 2753). (Compare G. Kossler and Penny, Zeits. f. physiol. Chem. **17**, 126.)

III. Bader (Zeits. f. analyt. Chem. **31**, 58) estimates phenol by direct titration with normal caustic soda, using trinitrobenzene as an indicator. Most phenols, however, give strongly coloured solutions when dissolved in alkalis, and this method has accordingly only a very limited application, and needs no further discussion.

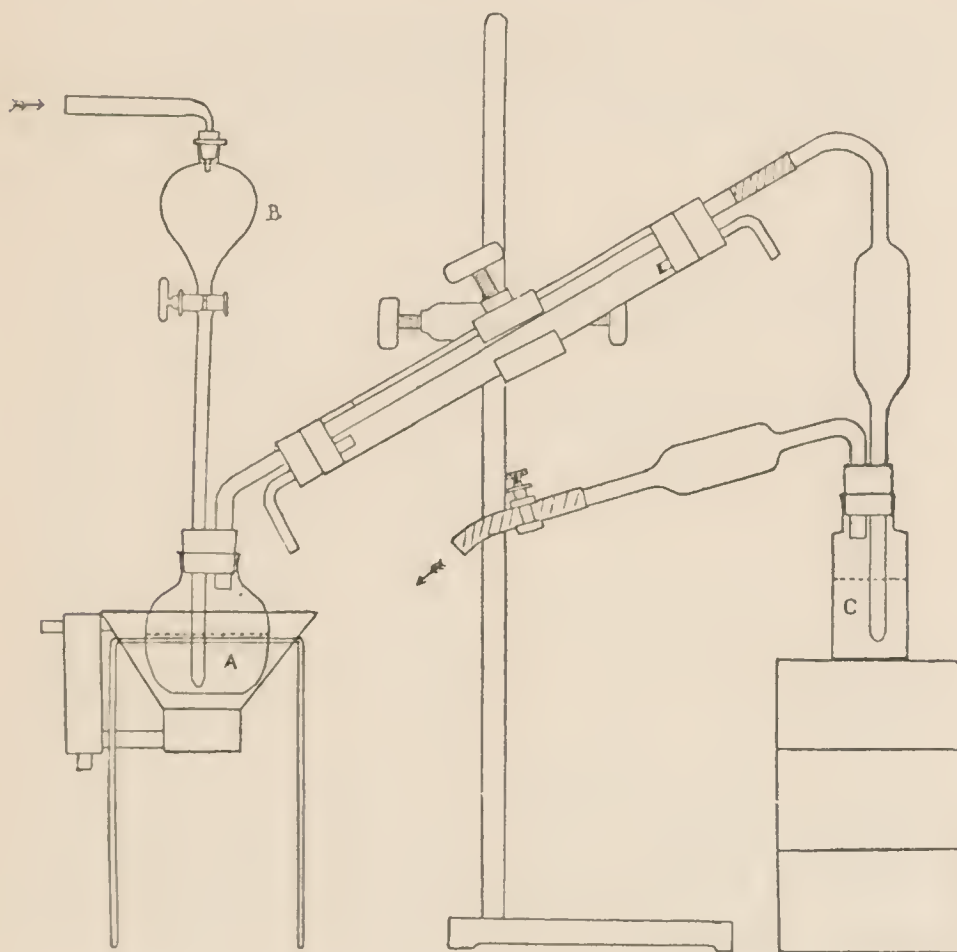
The methods hitherto generally adopted for estimating phenols fall then entirely under the first two headings. They have been subjected to criticism by Kleiner (Zeit. f. analyt. Chem. **23**, 13), and more recently by Mr. Carl E. Smith in a detailed report to a committee of the United States Pharmacopœia (Amer. Journ. Pharm., August 1898). The principal objection to their employment lies in the fact that a serious error occurs when the phenols are mixed even with small quantities of bodies capable of absorbing bromine or iodine, such as the hydrocarbons. This source of error is especially marked in the cases where an attempt is made to estimate the relative proportions of phenols in mixtures, such as phenol and the cresols, when the constituents only differ very slightly from one another in molecular weight, and also in attempting to estimate the amount of a phenol present in certain essential oils containing varying quantities of hydrocarbons, such as oil of thyme and oil of cloves.

Method and Apparatus.—A. W. Titherley (Trans. Chem. Soc. 1894, **66**, 504) described a few years ago a method by which the reagent sodium amide, $NaNH_2$, could be prepared pure and in considerable quantities without difficulty, and noted at the same time some of its reactions. Amongst others, it is known that it is capable of acting on bodies containing the hydroxyl group, replacing the hydrogen by sodium, evolving at the same time ammonia. Its action on water, alcohol, and phenol may be represented respectively by the three following equations:—



It is thus evident that for every hydrogen atom replaced in this way one molecule of ammonia is evolved. The principle of the method herein proposed consists in the treatment of a phenol in a solution of a substance having no action on sodium amide by an excess of this reagent, and estimating the ammonia evolved by the ordinary volumetric methods. Benzene was the liquid usually employed, and the apparatus is diagrammatically figured in the adjoining sketch.

The sodium amide (about 1 gm.) is finely ground, and washed two or three times by decantation with small quantities of benzene, and introduced into a 200 c.c. wide-mouthed flask (A), connected with an inverted condenser. About 50 or 60 c.c. of benzene, free from thiophen, is added, and the mixture is then boiled on a water-bath, while a current of dry air (free from CO_2), drawn by means of an aspirator or water-pump through a separating funnel (B), which dips under the surface of the liquid, is continually



sucked through the apparatus. This boiling is continued for some 10 minutes, so as to draw off the last traces of ammonia which adhere to the amide. About 20 c.c. of

normal sulphuric acid are then introduced into the ammonia absorption bottle (C), and the phenol dissolved in about six times its weight of benzene is introduced into the separating funnel. This is then allowed to drop slowly into the sodium amide and benzene mixture, which is kept the whole time in a state of constant ebullition, and connected with the aspirator or water-pump. As soon as the phenol has been all added, the funnel is washed with a little more benzene, and air is aspirated through the apparatus until no more ammonia remains unabsorbed. The benzene holds the ammonia somewhat pertinaciously, and $1\frac{1}{4}$ hour is generally required before the former is entirely driven out. Enough phenol is generally employed to require from 10—17 c.c. normal sulphuric acid for complete neutralisation of the ammonia evolved. At the end of the operation the excess of sulphuric acid is estimated by titration with normal sodium carbonate, methyl orange being generally used as

Quantity of substance taken.	Substance.	H ₂ SO ₄ required for neutrali- sation of NH ₃ evolved.	Quantity of substance found.	Error.
Grm.		C.c.	Grm.	
1·05	Phenol (pure)	11·2	1·05	0·00
1·03	"	10·7	1·05	+ 0·02
1·03	"	11·0	1·03	0·00
1·03	"	10·7	1·00	— 0·03
1·61	Cresol (ortho)	15·1	1·63	+ 0·02
2·08	Thymol	13·9	2·08	0·00
2·08	"	14·0	2·10	+ 0·02
2·09	"	13·7	2·05	— 0·04
2·09	"	13·6	2·04	— 0·05
2·09	"	13·7	2·05	— 0·04
2·09	"	14·0	2·10	+ 0·01
2·05	Guaiacol (cryst.)	16·4	2·03	— 0·02
2·06	"	16·6	2·06	0·00
2·06	"	16·6	2·06	0·00
2·06	"	16·5	2·05	— 0·01
2·06	"	16·4	2·03	— 0·02

indicator. In this way the total amount of ammonia evolved is readily estimated. The error in the titration should not deviate more than $\frac{2}{10}$ c.c. from the theoretical amount required. In order to obtain accurate results, the following special precautions must be observed:—

(i.) Both the phenol and the apparatus should be perfectly free from moisture, as water acts on sodium amide (see above). The methods of freeing the phenol from moisture will be discussed in detail below.

(ii.) Sufficient benzene must be employed. As some of the sodium salts formed are very insoluble in benzene, the apparatus is apt to become clogged unless a fairly large quantity of this liquid is employed.

(iii.) The benzene should be free from thiophen, otherwise minute quantities of sulphur compounds are apt to be carried over, which interfere with the delicacy of the indicator.

(iv.) Air should be aspirated through the apparatus for a sufficient length of time.

Xylene or toluene can be employed in the place of benzene, but in these cases a sand-bath instead of a water-bath must be employed. In some of the results given below, xylene or toluene were the liquids used.

Special Applications of the Method.

The Determination of the Relative Proportions of Different Phenols in Mixtures.

The method is, of course, not applicable to the determination of the relative proportions of more than two phenols. To test the method, mixtures were made of pure phenol and pure cresol in known proportions to imitate the commercial carboic acids. A series of experiments yielded the following results :—

—	Amount of Cresol.	Amount of Phenol.	H ₂ SO ₄ required to neutralise NH ₃ evolved.	Theoretical amount of H ₂ SO ₄ required.	"Hydroxyl" Value.
(a)	1·130	0·333	13·7 c.c.	13·5 c.c.	9·35
(b)	0·949	0·497	14·0 "	13·8 "	9·68
(c)	0·694	0·570	12·5 "	12·4 "	9·88
(d)	0·618	0·858	15·1 "	14·9 "	10·23

By the "hydroxyl value" is meant the number of c.c. of standard sulphuric acid solution that are necessary to neutralise the ammonia given off when 1 gram. of the substance (either simple substance or mixture) is treated with an excess of sodium amide under the conditions of an experiment. The hydroxyl value of pure phenol would be, therefore, $\frac{100}{9\cdot4}$ or 10·63, that of pure cresol $\frac{100}{10\cdot8}$ or 9·26, that is to say, the ammonia given off by 1 gram. of phenol would require 10·63 c.c. for neutralisation, that given off by the corresponding amount of cresol 9·26. Mixtures of phenol and cresol would have values lying between these two limits. A table is subjoined giving this hydroxyl value

for various mixtures of phenol and cresol, and it will be seen that an error of about 0·1 in this value can cause an error of about 10 per cent. in the relative proportions of the phenol and cresol. Whilst, therefore, the method gives a fairly accurate estimation of the total phenols present, only a rough approximation is obtainable of the relative proportions of such mixtures as phenol and cresol, where the difference in the molecular weights is small.

Percentage of Phenol.	Percentage of Cresol.	Hydroxyl Value.
100	0	10·63
90	10	10·49
80	20	10·35
70	30	10·21
60	40	10·08
50	50	9·92
40	60	9·76
30	70	9·67
20	80	9·53
10	90	9·37
0	100	9·26

In the examples of mixtures analysed, the relative proportions taken of phenol and cresol respectively are approximately (a) 20 and 80, (b) 35 and 65, (c) 45 and 55, (d) 20 and 80 per cent. From the "hydroxyl" values found, the relative proportions as read from the above table are (a) 10 and 90, (b) 30 and 70, (c) 45 and 55, (d) 30 and 70 per cent. A commercial carbolic acid analysed gave the following result: 1·50 grm. gave off NH_3 , requiring 15·5 c.c. H_2SO_4 for neutralisation. Hydroxyl value found, 10·33.

This corresponds to 80 per cent. phenol, 20 per cent. cresol.

Boiling Point of Fractions of Guaiacol.	Percentage.
204—205	17·7
205—206	14·6
206—207	11·4
207—208	12·9
208—209	11·3
209—210	6·6
210—211	6·0
211—212	6·0
212—214	5·0
214—216	6·6

Guaiacol from Wood Tar.—Guaiacol from wood tar is a liquid containing a mixture of guaiacol $\text{C}_6\text{H}_4(\text{OH})(\text{OCH}_3)$

and creosol $C_6H_3(CH_3)(OH)(OCH_3)_2$, two homologues which cannot be entirely separated by fractional distillation (Mendelsolm, Dissertation, Berlin, 1877). The respective boiling points of these two bodies are $205.1^\circ C.$ and 221° — $222^\circ C.$ In order to test the method of analysis, a sample of wood tar guaiacol was fractionated, and the separate fractions analysed to determine the relative proportions of phenol and creosol.

It was observed that the sample contained small quantities of water, which pertinaciously distilled over, with even some of the higher fractions. Each fraction was therefore analysed, both as originally obtained, and after drying over fused sodium sulphate for several days. It will be shown that this drying reagent only removes the last traces of moisture with very great difficulty. The results, however, show a clear gradation in the composition of the fractions as we pass from the lower to the higher.

Boiling Points of undried Fractions.	Amount of substance taken.	H ₂ SO ₄ used.	Hydroxyl Value.
204—205	1.45	13.6 c.c.	9.35
205—206	1.65	15.3 "	9.27
206—207	1.82	15.5 "	8.52
207—208	1.66	14.1 "	8.49
208—209	1.61	13.4 "	8.32
209—210	1.84	14.9 "	8.37
210—211	1.97	16.5 "	8.38
211—212	2.29	18.6 "	8.18
212—214	2.20	17.0 "	7.73

Dried Fractions.	Quantity used.	H ₂ SO ₄ for neutralisation.	Hydroxyl Value.
204—205	2.26	18.4 c.c.	8.14
205—206	2.10	17.2 "	8.19
206—207	2.15	17.4 "	8.09
207—208	1.60	13.0 "	8.09
208—209	2.11	16.4 "	7.77
209—210	1.65	12.5 "	7.57
210—211	2.08	15.9 "	7.64
211—211	1.82	14.0 "	7.68
212—214	1.42	10.7 "	7.53
214—216	1.62	12.0 "	7.41

Hydroxyl value for creosol 7.25
 " " guaiacol 8.06

From the above table, it will be seen that the fractions up to 208 contain very small amounts of the higher homologue. The fractions 208—211 are of nearly constant composition, and contain about equal parts of guaiacol and

creosol, whilst the highest fraction contains about 80 per cent. of the higher homologue. It will also be observed that the amount of water decreases rapidly after the two lowest fractions. The above tables indicate sufficiently how the composition of a mixture may be ascertained by this method of analysis.

Estimation of Thymol in Oil of Thyme.—For the purpose of control, an artificial mixture was first made by dissolving thymol in oil of turpentine.

A mixture weighing 8.087 gm., containing 2.183 gm. of thymol, gave off NH_3 , requiring 14.8 c.c. H_2SO_4 for neutralisation.

Percentage of thymol taken, 26.9. Percentage found, 27.4.

Three commercial oils, designated as first, second, and third quality, were then analysed :—

First quality :—

2.35 gm. undried, required	8.5 c.c. H_2SO_4
2.19 „ dry, „	5.5 c.c.
Percentage of thymol found	37.6
„ water „	2.4

Second quality :—

2.48 gm., dried, required	4.3 c.c. H_2SO_4
2.35 „ undried, required	7.7
Percentage of thymol found	26.0
„ water „	1.8

Third quality :—

2.35 gm., dried, required	3.1 c.c. H_2SO_4
2.31 „ undried, required	7.6
Percentage of thymol found	19.8
„ water „	2.3

Estimation of Eugenol in Oil of Cloves.—For the purpose of control, an artificial mixture was first prepared by dissolving some pure eugenol in oil of turpentine.

A mixture weighing 11.58 gm. containing 1.90 gm. eugenol required for neutralisation of NH_3 evolved 11.6 c.c. H_2SO_4 .

Percentage of eugenol taken	16.4
„ „ found	16.4

2.41 gm. of a sample of oil of cloves required 12 c.c. H_2SO_4 to neutralise NH_3 evolved.

Amount of eugenol present = 1.87 gm., corresponding to 77.7 per cent.

Estimation of Water in Phenols.—It has several times been mentioned above that the method is applicable to the estimation of moisture in phenols. A series of experiments was carried out with pure phenol to estimate the accuracy of the method, and to determine what water-withdrawing agents were best suited for the purpose. The phenol was always dried in benzene solution. Ordinary phenol combines with water of crystallisation, and is on this account somewhat difficult to thoroughly dry. It was found that fused sodium sulphate removes the last one per cent. of moisture only very slowly. Fused sodium acetate is, however, well adapted for the removal of the last traces of moisture.

Copper sulphate, on the other hand, partly combines with the phenol.

Experiments—

(a.) 1.176 gm. phenol containing 0.022 gm. moisture required 14.0 c.c. H_2SO_4 to neutralise the NH_3 evolved; 1.175 gm. dry should require 12.5 c.c.

The amount of water found as calculated from experiment = 0.02 gm.

(b.) 1.153 gm. of phenol with 0.041 gm. water were dissolved in benzene and dried over fused Na_2SO_4 and allowed to stand three days.

13.6 c.c. H_2SO_4 were required to neutralise the NH_3 evolved.

Theoretical quantity for 1.153 gm. phenol alone = 12.3.

The phenol still contained after standing over Na_2SO_4 0.023 gm. moisture.

(c.) 1.154 gm. phenol containing 0.039 gm. water were allowed to stand in benzene solution over fused Na_2SO_4 three days.

H_2SO_4 required to neutralise NH_3 evolved = 13.5 c.c.
1.154 gm. phenol requires 12.2.

Amount of water still in phenol = 0.023 gm.

Potassium carbonate forms a compound with phenol, and cannot therefore be used as a drying agent.

(d.) 1.108 gm. phenol with 0.055 gm. water were allowed to stand *one night* over fused sodium acetate.

H_2SO_4 required to neutralise NH_3 evolved = 11.6 c.c.

Theoretical for 1.108 gm. phenol = 11.7.

Sodium acetate is therefore a suitable drying agent.

(e.) 1.030 gm. phenol with 0.044 gm. water after standing over anhydrous CuSO_4 required 7 c.c. to neutralise NH_3 evolved.

1.030 gm. phenol require 10.9 c.c.

Another experiment gave a similar result.

Copper sulphate evidently, therefore, partly combines with the phenol.

This method for estimating phenols has perhaps a wider application than any of the previously employed processes, owing to the fact that the result is not interfered with by the presence of hydrocarbons. For this reason it can be applied to the estimation of phenols in a large number of essential oils, &c. Sodium amide also acts on ketones, amines, &c. (*vide* Titherley, Trans. Chem. Soc. 1897, 460). These bodies, however, can be readily separated from phenols by various reagents, such as sodium bisulphite, acids, &c.

A large number of the analyses detailed in the above paper were carried out by Mr. R. W. Kennedy.



